

FS/K-18804/APhotosensitive compositions

The present invention relates to a liquid photosensitive composition, to a process for the production of three-dimensional objects from said liquid composition, and to a process for the production of ceramic shells for investment casting.

A standard method of producing three-dimensional cast metal objects requires making a prototype from wax, plastic foams (e.g. polystyrene) or other fusible synthetic resin mixtures, which prototype is then coated with a mixture of ceramic materials. When the ceramic coating is subsequently fired, the wax or plastic model decomposes. The desired metal object can then be produced by casting the metal in the ceramic negative mould. This process is known as investment casting.

The traditional production of the models made from wax or fusible plastics materials, partly by hand, for use in investment casting is very time-consuming and expensive. The production of three-dimensional objects from liquid light-sensitive resins by stereolithography is disclosed in US patent specification 4 575 330. However, the photosensitive mixture disclosed therein - a modified acrylate - is not suitable for investment casting, as the thermal expansion of the cured moulding when firing the ceramic is too great, ultimately resulting in cracking of the ceramic shell.

Photosensitive compositions suitable for investment casting consisting of a poly(meth)acrylate resin dissolved in a liquid poly(meth)acrylate, a reactive diluent, a photoinitiator and a thermoplastic oligomer, are disclosed in US patent specification 4 844 144. However, these compositions have a rather low photosensitivity, i.e. high exposure energies are required for curing. Moreover, the step of firing the ceramic shell surrounding the models prepared from these compositions must be carried out under precisely defined conditions, i.e. the moulding has to be heated stepwise over a considerable period of time by means of a temperature program, resulting in process times of 48 hours and longer and hence in substantial production problems.

It has now been found that a liquid resin composition comprising an epoxy di-

(meth)acrylate and/or a urethane di(meth)acrylate, a bifunctional (meth)acrylate, a photo-initiator and an inert diluent, and which may further comprise monofunctional and trifunctional (meth)acrylates as well as N-vinylpyrrolidone or N-vinylcaprolactam, has a high photosensitivity, and that the models prepared therefrom by stereolithography can be readily used for investment casting.

Accordingly, the invention relates to a liquid photosensitive composition comprising, based on the total composition,

- (a) 10-50 % by weight of an epoxy di(meth)acrylate and/or a urethane di(meth)acrylate,
 - (b) 15-45 % by weight of one or more than one bifunctional (meth)acrylate having a molecular weight in the range from 150 to 450,
 - (c) 0-20 % by weight of a trifunctional (meth)acrylate,
 - (d) 0-10 % by weight of N-vinylpyrrolidone or N-vinylcaprolactam,
 - (e) 0-10 % by weight of a monofunctional (meth)acrylate,
 - (f) 15-30 % of one or more than one inert diluent selected from the group consisting of C₂-C₁₂alcohols, C₄-C₁₂alkanediols, C₄-C₁₂dialkylketones, polyalkylene glycols, di- or triterpenes, hydroxyalkyl esters of β -hydroxycarboxylic acids, caprolactams, chloro-paraffins and diphthalates, diadipates or citrates, obtainable by reacting phthalic acid, adipic acid or citric acid with C₁-C₁₂alcohols, and
 - (g) 3-7 % by weight of a photoinitiator.
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The novel composition preferably comprises, based on the entire composition, 25-45 % by weight of component (a), 20-45 % by weight of component (b) and 5-20 % by weight of component (c).

The reaction products of diglycidyl compounds, typically diglycidyl ethers of diols, with (meth)acrylic acid, are termed epoxy di(meth)acrylates.

Di(meth)acrylates suitable for use as component (a) of the novel compositions are typically the acrylates obtainable by reacting unsubstituted or substituted diglycidyl ethers of bisphenol A or bisphenol F with (meth)acrylic acid. Such monomeric or oligomeric di(meth)acrylates are known and some are commercially available. It is preferred to use the diglycidyl diacrylate of bisphenol A.

The urethane di(meth)acrylates suitable for use as component (a) of the novel compositions are also known to those skilled in the art and can be prepared in known

manner, typically by reacting a dihydroxy-terminated polyurethane with acrylic or methacrylic acid to give the corresponding urethane di(meth)acrylate, or by reacting a diisocyanate-terminated prepolymer with hydroxy(meth)acrylates to give the urethane di(meth)acrylate. Suitable processes are disclosed in EP patent applications 114 982 and 133 908. The molecular weight of such acrylates is usually in the range from 400 to 10 000, preferably from 500 to 7000.

It is preferred to use those urethane di(meth)acrylates which have a molecular weight of 500-7000 and have been prepared from aliphatic educts.

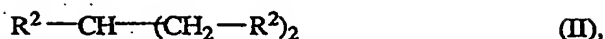
Compounds suitable for use as component (b) include the diacrylate and dimethacrylate esters of aliphatic, cycloaliphatic or aromatic diols, typically 1,3-butyleneglycol, 1,4-butanediol, neopentyl glycol, 1,6-hexanediol, diethylene glycol, triethylene glycol, tetraethylene glycol, tripropylene glycol, ethoxylated or propoxylated neopentyl glycol, 1,4-dihydroxymethylcyclohexane, 2,2-bis(4-hydroxycyclohexyl)propane, bis(4-hydroxycyclohexyl)methane, hydroquinone, 4,4'-dihydroxybiphenyl, bisphenol A, bisphenol F, bisphenol S, ethoxylated or propoxylated bisphenol A, ethoxylated or propoxylated bisphenol F or ethoxylated or propoxylated bisphenol S.

Such di(meth)acrylates are likewise known and some are commercially available, typically those sold by the SARTOMER Company under the product names SR-348 for ethoxylated bisphenol A dimethacrylate and SR-349 for ethoxylated bisphenol A diacrylate.

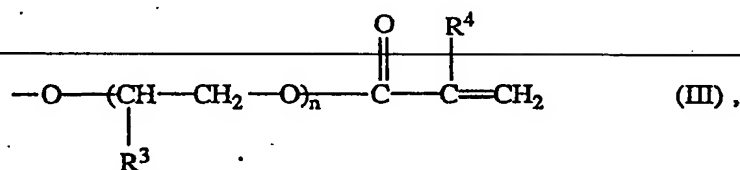
It is preferred to use a di(meth)acrylate of ethoxylated bisphenol A and/or neopentyl glycol di(meth)acrylate as component (b).

Compounds suitable for use as component (c) are typically triacrylates or trimethacrylates of formula I or II

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wherein R^1 is a hydrogen atom, methyl or hydroxyl,
and R^2 is a radical of formula III



wherein n is 0 or a number from 1 to 3, and R^3 and R^4 are each independently of the other a hydrogen atom or methyl.

Among the compounds of formulae I and II, those compounds of formula I, wherein R^1 is a methyl group and R^2 is a radical of formula III, wherein n is 0, are especially preferred.

Illustrative examples of compounds which may be used as component (c) are:

1,1,1-trimethylolpropane triacrylate or trimethacrylate, ethoxylated 1,1,1-trimethylolpropane triacrylate or trimethacrylate, pentaerythritol monohydroxy triacrylate or trimethacrylate. Such compounds are known and some are commercially available.

The compounds useful as component (c) preferably have a molecular weight of 250 to 500.

It is particularly preferred to use trimethylolpropane tri(meth)acrylate as component (c).

The novel compositions may contain as optional component (d) up to 10 % by weight of N-vinylpyrrolidone or N-vinylcaprolactam. It is preferred to use N-vinylpyrrolidone.

Component (e) of the novel compositions may be selected from the following compounds:

allyl acrylate, allyl methacrylate, methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, n-hexyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, n-octyl (meth)acrylate, n-decyl (meth)acrylate and n-dodecyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2- and 3-hydroxypropyl (meth)acrylate, 2-methoxyethyl (meth)acrylate, 2-ethoxyethyl (meth)acrylate and 2- or 3-ethoxypropyl (meth)acrylate, tetrahydrofurfurylmethacrylate, 2-(2-ethoxyethoxy)ethylacrylate, cyclohexyl methacrylate, 2-phenoxyethyl acrylate, glycidyl acrylate and isodecyl acrylate; Such products are also known and some are commercially available, as from SARTOMER.

2-Phenoxyethyl(meth)acrylate is especially preferred.

Exemplary inert diluents suitable for use as component (f) of the novel compositions are C_2 - C_{12} alcohols, including isopropanol, isobutanol or, preferably, tert-butanol, and C_4 - C_{12} alkanediols such as 2,4-dimethylpentane-2,4-diol, pinacol or, preferably, pinacolone. Further useful diluents are C_4 - C_{12} dialkylketones such as 2,2-dimethylpentan-3-one or, preferably, pinacolone and polyalkylene glycols, including diethylene, triethylene or tetraethylene glycol, dipropylene, tripropylene or tetrapropylene glycol or dibutylene glycol. Further suitable inert diluents are di- or triterpenes, including α -pinene, camphor, limonene or menthol, hydroxyalkyl esters of β -hydroxycarboxylic acids, such as 2,2-dimethyl-3-hydroxypropyl 2,2-dimethyl-3-hydroxypropionate, caprolactams such as ϵ -caprolactam, chloroparaffins, for example the chlorinated paraffin hydrocarbons sold by Hoechst AG under the registered trademark Hordalub[®], and diphthalates, diadipates or citrates obtainable by reacting phthalic acid, adipic acid or citric acid with C_1 - C_{12} alcohols.

As component (f) it is preferred to use tert-butanol, pinacol, pinacolone, dipropylene glycol, triethylene glycol, tripropylene glycol, α -pinene, camphor, limonene, menthol, caprolactam, 2,2-dimethyl-3-hydroxypropyl 2,2-dimethyl-3-hydroxypropionate, dimethyl adipate, diethyl phthalate, bis(2-methoxyethyl) phthalate, bis(2-ethylhexyl) phthalate.

As component (f) it is particularly preferred to use diethylene, triethylene or tetraethylene glycol, dipropylene, tripropylene or tetrapropylene glycol, dibutylene glycol, caprolactam, chloroparaffin, 2,2-dimethyl-3-hydroxypropyl 2,2-dimethyl-3-hydroxypropionate, and diphthalates or citrates obtainable by reacting phthalic acid or citric acid with C_3 - C_{12} alcohols, preferably bis(2-ethylhexyl) phthalate.

Any type of photoinitiator which, when irradiated suitably, forms free radicals can be employed as component (g) in the novel compositions. Typical known photoinitiators are benzoin, benzoin ethers, including benzoin, benzoin methyl ether, benzoin ethyl ether and benzoin isopropyl ether, benzoin phenyl ether and benzoin acetate, acetophenones, including acetophenone, α,α -dimethoxyacetophenone and α,α -dichloroacetophenone; benzil, benzil ketals, such as benzil dimethyl ketal and benzil diethyl ketal; anthraquinones, including 2-methylantraquinone, 2-ethylantraquinone, 2-tert-butylantraquinone, 1-chloroanthraquinone and 2-amylantraquinone, triphenylphosphine; benzoylphosphine oxides, for example 2,4,6-trimethylbenzoyldiphenylphosphine oxide (Luzirin TPO); benzophenones such as benzophenone and 4,4'-bis(N,N'-dimethylamino)-benzophenone; thioxanthenes and xanthenes such as 2-isopropylthioxanthone; acridine derivatives; phenazine derivatives; quinoxaline derivatives or 1-phenyl-1,2-propanedione, 2-O-benzoyl oxime; α -aminophenyl ketones such as 1-(4-methylthiophenyl)-2-methyl-2-morpholinobutan-1-one, or 1-hydroxyphenyl ketones, such as 1-hydroxycyclohexyl phenyl ketone, phenyl 1-hydroxyisopropyl ketone and 4-isopropylphenyl 1-hydroxyisopropyl ketone.

Also suitable are electron transfer initiators of the xanthone type, for example 2,4,5,7-tetraiodo-6-hydroxy-9-cyano-3H-xanthene-3-one which, together with suitable electron donors, have a high reactivity in the visible range of the spectrum.

Particularly suitable photoinitiators which are normally used in combination with a HeCd laser as radiation source are acetophenones, conveniently 2,2-dialkoxybenzophenones, and α -hydroxyphenyl ketones, for example 1-hydroxycyclohexyl phenyl ketone or 2-hydroxyisopropyl phenyl ketone (= 2-hydroxy-2,2-dimethylacetophenone).

Preferred photoinitiators are benzil dimethyl ketal, 1-(4-methylthiophenyl)-2-methyl-2-morpholinobutan-1-one, 2-isopropylthioxanthone and, most preferably, 1-hydroxycyclohexylphenylketone.

The novel compositions may also contain other photoinitiators of different sensitivity to radiation of emission lines of different wavelengths. The inclusion of such photoinitiators effects the better utilisation of a UV/VIS light source which radiates emission lines of different wavelength. It is advantageous to choose these other photoinitiators and to use them in such a concentration that a uniform optical absorption is produced with respect to the emission lines used.

If desired, the compositions of this invention may contain the customary additives, typically stabilisers such as UV stabilisers, polymerisation inhibitors such as hydroquinone monomethyl ether, release agents, wetting agents, flow control agents, sensitisers, antiprecipitants, surfactants, dyes, pigments or fillers.

The novel photosensitive compositions can be polymerised by irradiation with actinic light, typically with electron beams, X-rays, UV or VIS light, i.e. with radiation in the wavelength range from 280-650 nm. Particularly suitable light sources are HeCd, argon or nitrogen laser light as well as metal vapour and NdYAG lasers with multiple frequency.

Those skilled in the art will know that the appropriate photoinitiator for each selected light source must be chosen and, if necessary, sensitised. It has been found that the depth of penetration of the radiation into the polymerised composition and the processing rate are directly related to the absorption coefficient and the concentration of the photoinitiator. In stereolithography it is preferred to use those photoinitiators which generate the highest number of resulting free radicals and make possible the greatest depth of penetration into the compositions to be polymerised.

The invention further relates to a process for the production of three-dimensional objects from the novel liquid compositions by stereolithography, in which a layer of novel liquid composition is irradiated over the entire surface or in a predetermined pattern with a UV/VIS light source, such that within the irradiated areas a layer solidifies in a desired layer thickness, then a new layer of novel composition is formed on the solidified layer, which is likewise irradiated over the entire surface or in a predetermined pattern, and such that three-dimensional objects are formed from a plurality of solidified layers which adhere to one another by repeated coating and irradiation.

In this process it is preferred to use a laser light which is preferably computer-controlled.

A preferred utility of the three-dimensional objects produced by the process of this invention is as models for the investment casting technique. This technique comprises coating the cured plastic moulding with a ceramic layer and then gradually heating the ceramic-coated model to a temperature above 500 °C, preferably to a temperature in the range from c. 800-1200°C, and keeping this temperature for several hours, whereupon the plastic model decomposes completely. The residual ceramic shell is suitable for use as a negative mould for making moulded metal parts.

The plastic model produced by stereolithography is coated with ceramic by per se known methods, typically by immersing the model in a liquid mixture of ceramic materials and subsequently drying the coating. The model coated with a first ceramic layer is then preferably treated with quartz or zirconium sand and dried once more. This procedure is repeated several times to give a ceramic shell several mm thick.

In another embodiment of the invention, the plastic model is placed in a suitable container and the ceramic material is cast around the model in the container (flask casting).

The invention thus also relates to a process for producing ceramic shells for investment casting, which comprises coating or surrounding a plastic model prepared by stereolithography with ceramic, and subjecting the ceramic-coated plastic model to a burn-out at temperatures above 500°C until the plastic model has decomposed completely.

In a preferred embodiment of the invention the ceramic-coated plastic model is subjected to a vacuum treatment prior to the burn-out, thereby substantially reducing the duration of the process.

Thus the invention relates still further to a process for the production of a ceramic shell for investment casting, which comprises coating a plastic model prepared by stereolithography with ceramic, stoving the ceramic-coated plastic model under vacuum in the temperature range from ambient temperature to 150°C until the inert diluent has evaporated completely, and thereafter firing said ceramic-coated plastic model at temperatures above 500 °C until said plastic has decomposed completely.

The products prepared from the novel compositions by stereolithography are distinguished by good performance properties, in particular by superior definition of the ceramic shells after the burn-out.

The invention is illustrated by the following Examples.

Example 1: 40.4 g of the diglycidyl diacrylate of bisphenol A are mixed at 40°C with 20.7 g of the ethoxylated diacrylate of bisphenol A (Mw = 424, product SR-349 sold by the SARTOMER Company), 10 g of trimethylolpropane trimethacrylate, 4 g of 1-hydroxycyclohexyl phenyl ketone, 0.1 g of hydroquinone monomethyl ether and 16.6 g of bis(2-ethylhexyl) phthalate. The resultant homogeneous liquid mixture has a viscosity of 1510 mPa·s at 30°C.

The liquid is irradiated with a deflectable He/Cd laser beam to give a laser-cured polymer filament, the thickness of which is an indicator of the photosensitivity of the mixture. The thickness of the filament is 0.15 mm at an intensity of 20 mJ/cm², 0.29 mm at an intensity of 40 mJ/cm², 0.44 mm at 80 mJ/cm² and 0.52 mm at 160 mJ/cm².

In the tensile test according to DIN 53 371, a moulded product made from this composition and cured at an intensity of 40 mJ/cm² has a modulus of elasticity (green strength) of 7,6 N/mm².

After a full cure of this so-called green model by irradiation with UV/VIS light (c. 30 minutes, Hg lamp or fluorescent tube), the modulus of elasticity is 1440 N/mm². The elongation at break according to DIN 35 455 is 3.4 %.

To test the inventive composition for its suitability as fine casting resin, the following model is prepared from the resin composition:

The model consists of two non-concentric interlocking rings linked together by 6 supports. The model has a height of 42 mm and an outer diameter of 129 mm. It is finished at the bottom by a round hollow reinforcement which has a height of 6 mm and a width of 13 mm. The model has different wall thicknesses of 1 mm to 2.5 mm and weighs 77 g. The model is immersed for about half a minute in a commercial liquid ceramic mixture and afterwards dried in the air until the ceramic-coated model is just slightly moist. The ceramic-coated model is then treated with quartz sand and dried in the air. This procedure is repeated 15 times. The ceramic shell surrounding the model has a thickness of c. 6-8 mm.

The ceramic-coated plastic model is heated in a programmed oven for 8 hours from 100°C to 800°C, in the course of which burn-out the model decomposes completely. After cooling to ambient temperature, the ceramic shell is examined for cracks under a magnifying glass. The degree of intactness is evaluated using a scale from 1-5. Shells with ratings of 1-3 can be used in the subsequent casting process:

- 1: no cracking - successful burn-out
- 2: very minor cracking - shell easily reparable

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- 3: moderate cracking - shell reparable
- 4: severe cracking - portions of shell irreparably fragmented
- 5: total failure - entire shell fragmented.

Two of the above described models are prepared from 2 kg of the resin composition in a SLA-250 machine supplied by 3D-Systems, and subsequently immersed in a liquid ceramic mixture and sanded. The procedure is repeated several times to give a 8 mm thick ceramic shell. The ceramic-coated plastic models are heated in a programmed oven for 8 hours from 100°C to 800°C, in the course of which burn-out the models decompose completely. The ceramic shells so obtained are given the rating 2.

Examples 2-11: In accordance with the general procedure described in Example 1, plastic models are prepared from the compositions listed in Table 2, coated with ceramic and fired in an oven. The properties of the cured models and of the ceramic shells are shown in Table 2.

Table 1: Compositions of Examples 1-11 (amounts in g)

Examples	1	2	3	4	5	6	7	8	9	10	11
diglycidyl diacrylate of bisphenol A	40.40	44.27	30.40	40.40	40.40	40.40	29.60	29.60			29.85
ethoxylated dimethacrylate of bisphenol A	20.70	22.70	15.50	20.70	20.70	20.70	4.10	4.10			4.00
trimethylolpropane trimethacrylate	10.0	10.9	7.5	10.00	10.00	10.00	4.10	4.10	4.50	4.50	4.00
N-vinylpyrrolidone	4.1	4.5	3.1	4.1	4.1	4.1	5.8	5.8			5.0
phenoxy ethyl acrylate	4.1	4.5	3.1	4.1	4.1	4.1	4.1	4.1			5.0
1-hydroxycyclohexyl phenyl ketone	4.0	4.0	3.0	4.0	4.0	4.0	5.0	5.0	4.9	4.9	5.0
hydroquinone monomethyl ether	0.1	0.13	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.15
urethane diacrylate C 9504 (Sartomer)			12.40						32.60	32.60	
butanediol diacrylate									8.90	8.90	
ethoxylated diacrylate of bisphenol A							20.70	20.70	32.50	32.50	20.00
trimethylolpropane triacrylate							10.00	10.00			9.00
neopentyl glycol dimethacrylate											6.00
Polyurax® U 1102 *)			24.90								
bis(2-methoxyethyl)phthalate				16.40							
Hordalub® 80 HT **)					16.40						
caprolactam						16.40					
bis(2-ethylhexyl)phthalate	16.6	9.0				16.40	16.50	16.50	16.50	16.50	17.00

*) polymeric polyol sold by BP Chemicals

**) chloroparaffin sold by Hoechst

Table 2:

Example	1	2	3	4	5	6	7	8	9	10	11
Viscosity of the liquid composition at 35°C [mPa · s]	460	700	1720	379	969	748	407	556	818	1040	458 (30 °C)
Thickness of the polymer filament after irradiation with 20 mJ/cm ² [mm]	0.15	0.15		0.19	0.17	0.22	0.17	0.24		0.22	
40 mJ/cm ²	0.29	0.29	0.31	0.30	0.32	0.36	0.27	0.34	0.27	0.33	0.23
80 mJ/cm ²	0.44	0.43	0.42	0.42	0.42	0.50	0.39	0.47	0.41	0.46	0.34
160 mJ/cm ²	0.52	0.57	0.52	0.55	0.56	0.65	0.51	0.57	0.52	0.56	0.47
module of elasticity [N/mm ²] (after irradiation at 40 mJ/cm ²)	7.6	22.1		3.0	18.0	18.0	25.0	34.0	1.8	3.4	2.3
Properties after cure with UV/VIS light											
module of elasticity [N/mm ²]	1440	1860	782	1365	1430	1361	1500	1360	450	370	1564
elongation at break [%]	3.4	2.9	6.7	5.7	5.2	5.0	4.7	6.8	9.0	12.0	5.0
quality of the fired ceramic shell*)	2	3	2	1.5-2	1.5	1.5-2	1	2	1.5	2	

*) 1: no cracking - successful burn-out
 2: very minor cracking - shell easily repairable
 3: moderate cracking - shell repairable

Examples 12-33: The compositions of Examples 12-33 shown in Tables 3 and 5 are prepared and tested in accordance with the general procedure described in Example 1. The compositions of Examples 12-17 and 24-33 are irradiated as in Example 1 with a He/Cd laser beam, whereas in Examples 18-23 a deflectable Ar-UV laser beam is used. The results of the tests are reported in Tables 4 and 6.

The liquid compositions so prepared are cured between two glass plates by irradiation with UV/VIS light (c. 30 min, Hg lamp or fluorescent tube). Afterwards the cured resin boards are cut into specimens of 70-150 mm in length, 20-33 mm wide and 2 mm thick. These specimens are coated as described in Example 1 with two layers of a liquid ceramic mixture, using zirconium sand (100 mesh) for sanding. Then, using fused silica (50 mesh) for sanding, five further ceramic layers are applied. After drying the resin specimens, the ceramic layer is c. 5-6 mm thick. The coated specimens are heated in a programmable oven to 900°C for 13 hours and thereafter kept for 1 hour at this temperature, in the course of which the ceramic shell obtains its final strength. The plastic specimens have decomposed completely in the course of the burn-out. After cooling to ambient temperature, the ceramic shells are examined under a magnifying glass. The results are reported in Tables 4 and 6.

Table 3: Compositions of Examples 12-23 (amounts in g)

[illegible]

Example	12	13	14	15	16	17	18	19	20	21	22	23
Viscosity of the liquid composition at 35 °C [mPa · s]	670	683	738	798	895	965	765	770	770	770	795	760
Thickness of the polymer filament after irradiation with 20 mJ/cm ² [mm]	0.12 0.24 0.34 0.44	0.13 0.25 0.36 0.47	0.13 0.24 0.35 0.46	0.15 0.26 0.36 0.47	0.13 0.25 0.35 0.46	0.13 0.24 0.35 0.46	0.29 0.42 0.65 0.79	0.26 0.36 0.51 0.60	0.24 0.32 0.43 0.52	0.24 0.46 0.73 1.05	0.15 0.22 0.32 0.45	0.18 0.26 0.36 0.45
modulus of elasticity [N/mm ²] after irradiation with 40 mJ/cm ² after irradiation with 80 mJ/cm ²	7.5 72.6	5.9 56.2	6.7 61.7	10.2 64.5	8.0 57.6	9.0 90.1	5.5 44.8	7.5 46.2	11.4 53.4	4.8	4.7 28.1	3.6 19.7
Properties after cure with UV/VIS light modulus of elasticity [N/mm ²] elongation at break [%] quality of the fired ceramic shell	1430 3.8 1	1328 5.7 1	1369 7.7 1	1436 6.5 1	1450 6.1 1	1523 5.6 1	1310 7.5 1	1440 6.6 1	1490 4.4 1	880 7.0 1	1200 5.7 1	1200 4.9 1

[illegible]

Example	24	25	26	27	28	29	30	31	32	33
Viscosity of the liquid composition at 35 °C [mPa · s]	351	127	409	414	91	326	180	533	84	372
Thickness of the polymer filament after irradiation with 20 ml/cm ² [mm] 40 ml/cm ² 80 ml/cm ² 160 ml/cm ² 320 ml/cm ²	0.23 0.34 0.43	0.30 0.40 0.29	0.12 0.24 0.34 0.44	0.15 0.24 0.33 0.43	0.23 0.34 0.42	0.19 0.23 0.31 0.44	0.15 0.22 0.32 0.44	0.27 0.31 0.44		0.25 0.37 0.53
modulus of elasticity [N/mm ²] after irradiation with 40 ml/cm ² after irradiation with 80 ml/cm ²	3.4 18.1	3.0 32.3	4.3 21.9	4.6 34.5	4.0 37.7	10.1 95.8	6.4 43.8	5.4 40.6		
Properties after cure with UV/VIS light modulus of elasticity [N/mm ²] elongation at break [%] quality of the fired ceramic shell	453 7.8 1	1081 3.3 1	837 9.0 1	1996 3.7 1	3675 3.2 1	2130 3.6 1	2173 4.3 1	2112 3.8 1	1 1	1

What is claimed is:

1. A liquid photosensitive composition comprising, based on the entire composition
(a) 10-50 % by weight of an epoxy di(meth)acrylate and/or a urethane di(meth)acrylate,
(b) 15-45 % by weight of one or more than one bifunctional (meth)acrylate having a molecular weight in the range from 150 to 450,
(c) 0-20 % by weight of a trifunctional (meth)acrylate,
(d) 0-10 % by weight of N-vinylpyrrolidone or N-vinylcaprolactam,
(e) 0-10 % by weight of a monofunctional (meth)acrylate,
(f) 15-30 % of one or more than one inert diluent selected from the group consisting of C₂-C₁₂alcohols, C₄-C₁₂alkanediols, C₄-C₁₂dialkylketones, polyalkylene glycols, di- or triterpenes, hydroxyalkyl esters of β -hydroxycarboxylic acids, caprolactams, chloro-paraffins and diphthalates, diadipates or citrates, obtainable by reacting phthalic acid, adipic acid or citric acid with C₁-C₁₂alcohols, and
(g) 3-7 % by weight of a photoinitiator.
2. A composition according to claim 1 which comprises, based on the entire composition, 20-45 % by weight of component (a), 20-45 % by weight of component (b) and 5-20 % by weight of component (c).
3. A composition according to claim 1, wherein component (a) is the diglycidyl diacrylate of bisphenol A.
4. A composition according to claim 1, wherein component (b) is a di(meth)acrylate of ethoxylated bisphenol A and/or neopentyl glycol di(meth)acrylate.
5. A composition according to claim 1, wherein component (c) is trimethylolpropane tri(meth)acrylate.
6. A composition according to claim 1, wherein component (e) is phenoxyethyl (meth)acrylate.
7. A composition according to claim 1, wherein component (f) is an inert diluent selected from the group consisting of tert-butanol, pinacone, pinacolone, dipropylene glycol, triethylene glycol, tripropylene glycol, α -pinene, camphor, limonene, menthol,

caprolactam, 2,2-dimethyl-3-hydroxypropyl 2,2-dimethyl-3-hydroxypropionate, dimethyl adipate, diethyl phthalate, bis(2-methoxyethyl) phthalate, and bis(2-ethylhexyl) phthalate.

8. A composition according to claim 1, wherein component (f) is an inert diluent selected from the group consisting of diethylene, triethylene or tetraethylene glycol, dipropylene, tripropylene or tetrapropylene glycol, dibutylene glycol, caprolactam, chloroparaffin, 2,2-dimethyl-3-hydroxypropyl 2,2-dimethyl-3-hydroxypropionate, and diphthalates or citrates obtainable by reacting phthalic acid or citric acid with C₃-C₁₂alcohols.

9. A composition according to claim 1, wherein component (g) is selected from the group consisting of benzil dimethyl ketal, 1-(4-methylthiophenyl)-2-methyl-2-morpholinobutan-1-one, 2-isopropylthioxanthone or 1-hydroxycyclohexyl phenyl ketone.

10. A composition according to claim 1, wherein component (g) is 1-hydroxycyclohexyl phenyl ketone.

11. A process for the production of three-dimensional objects from the novel liquid compositions by lithographic methods, wherein a layer of novel liquid composition is irradiated over the entire surface or in a predetermined pattern with a UV/VIS light source, such that within the irradiated areas a layer solidifies in a desired layer thickness, then a new layer of novel composition is formed on the solidified layer, which is likewise irradiated over the entire surface or in a predetermined pattern, and such that three-dimensional objects are formed from a plurality of solidified layers which adhere to one another by repeated coating and irradiation.

12. A process according to claim 11, wherein a laser beam, preferably a computer-controlled laser beam, is used as source of irradiation.

13. A process for the production of a ceramic shell for investment casting, which comprises coating or surrounding a plastic model prepared by stereolithography according to claim 11 with ceramic, and thereafter firing the ceramic-coated plastic model at temperatures above 500°C until said plastic has decomposed completely.

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14. A process for the production of a ceramic shell for investment casting, which comprises coating a plastic model prepared by stereolithography according to claim 11 with ceramic, stoving the ceramic-coated plastic model under vacuum in the temperature range from ambient temperature to 150°C until the inert diluent has evaporated completely, and thereafter firing said ceramic-coated plastic model at temperatures above 500 °C until said plastic has decomposed completely.

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FD 4.3/SP/cw*

FS/K-18804/APhotosensitive compositionsAbstract of the Disclosure

Liquid photosensitive compositions comprising, based on the entire composition

(a) 10-50 % by weight of an epoxy di(meth)acrylate and/or a urethane di(meth)acrylate,

(b) 15-45 % by weight of one or more than one bifunctional (meth)acrylate having a molecular weight in the range from 150 to 450,

(c) 0-20 % by weight of a trifunctional (meth)acrylate,

(d) 0-10 % by weight of N-vinylpyrrolidone or N-vinylcaprolactam,

(e) 0-10 % by weight of a monofunctional (meth)acrylate,

(f) 15-30 % of one or more than one inert diluent selected from the group consisting of C₂-C₁₂alkohols, C₄-C₁₂alkanediols, C₄-C₁₂dialkylketones, polyalkylene glycols, di- or triterpenes, hydroxyalkyl esters of β -hydroxycarboxylic acids, caprolactams, chloro-paraffins and diphthalates, diadipates or citrates, obtainable by reacting phthalic acid, adipic acid or citric acid with C₁-C₁₂alkohols, and

(g) 3-7 % by weight of a photoinitiator,

can be polymerised by actinic radiation and are particularly suitable for producing three dimensional objects by stereolithography. These objects may be used as models for producing ceramic shells for the investment casting technique.

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